

Effect of Solvents in Radiation-Induced Grafting of 4-Vinyl Pyridine onto Fluorinated Ethylene Propylene Copolymer

S. K. Rath, A. Palai, Swati Rao, L. Chandrasekhar, M. Patri

Naval Materials Research Laboratory, Ambernath, Maharashtra 421506, India

Received 12 October 2006; accepted 29 December 2007

DOI 10.1002/app.28022

Published online 19 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A wide range of solvents have been examined to find their effect on radiation-induced grafting of 4-vinyl pyridine onto fluorinated ethylene propylene copolymer by simultaneous irradiation technique. The effect of solvent on percentage of grafting has been monitored by varying monomer concentration and total dose of radiation. Further grafting results have been correlated with the solubility parameter of the solvent and solvent mixtures. Evidence of grafting has been based on characterization of grafted samples in terms of FTIR, EDAX, X-ray mapping, thermogravimetric analysis, and dynamic mechanical analysis. Depth profiling of a few

representative grafted films were studied by viewing the cross-sectional distribution of elemental nitrogen using SEM-EDAX. The results suggest that with increase in grafting the grafting front propagates from the surface toward bulk, thus establishing the frontal mechanism of radiation grafting. Furthermore, the grafted films were characterized for their surface properties using contact angle goniometry. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 4065–4071, 2008

Key words: graft copolymerization; FEP; solubility parameter; 4-vinyl pyridine

INTRODUCTION

Graft copolymerization is the most powerful and general method in effecting modification of polymers and is widely used in the production of commercially useful polymers. Synthesis of proton exchange membranes for use as electrolytes in fuel cell is one of the most prominent applications.^{1–11} Significant efforts have also been made to develop anion exchange membranes by radiation-induced graft copolymerization of vinyl monomers such as 4-vinyl pyridine, 2-vinyl pyridine, and vinyl benzyl chloride onto various polymer films by using direct and preirradiation methods. Anion exchange membranes prepared by grafting of 4-vinyl pyridine onto films such as PTFE,^{12–13} PE,¹⁴ PP,¹⁵ ETFE,¹⁶ PVC,¹⁷ followed by quaternization with alkyl halide has also been reported.

Grafting efficiency in radiation-induced graft copolymerization by simultaneous irradiation technique depends upon¹⁸ monomer concentration, total dose, nature of the polymer and monomer, nature of the solvent or diluents, etc. Solvents are basically used in radiation-induced graft copolymerization to bring about swelling of the base polymer and enhance the monomer accessibility to grafting sites.¹⁹ Accordingly, correct choice of diluents is one of the essential elements toward the success of radiation-induced grafting process.²⁰ The

effect of solvents on the radiation-induced graft copolymerization reactions during membrane preparation has been subjected to many studies.^{21–24} In an exhaustive study, Garnet and Martin²⁵ reported the effect of a large number of solvents on simultaneous radiation-induced graft copolymerization of 2-vinyl pyridine, 4-vinyl pyridine, and 2-methyl-5-vinyl pyridine onto cellulose. Solvents having functional groups containing nitrogen or/and oxygen ensured high grafting efficiency. Kaur et al.²⁶ have evaluated the effect of various alcohols and binary mixture of alcohols and water toward grafting of 4-vinyl pyridine onto FEP by preirradiation technique.

In this article, the effect of various solvents and binary mixture of solvents on grafting of 4-vinyl pyridine onto FEP by simultaneous irradiation technique has been studied. The effect of monomer concentration and total dose on grafting in presence of different solvents has been evaluated. Selected grafted samples have been characterized by using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and scanning electron microscopy — energy dispersive spectroscopy (SEM-EDAX).

EXPERIMENTAL

Materials and methods

Teflon-FEP film (75 μm thickness) was obtained from Du Pont (Wilmington, DE); 4-vinyl pyridine (Alfa Aesar, Heysham, England) was freshly distilled

Correspondence to: M. Patri (mrpatri@rediffmail.com).

before use. Tetrahydrofuran (THF), dioxane, methanol, acetone, benzyl alcohol, nitromethane, cyclohexanol, methyl ethyl ketone (MEK), and water were duly purified and distilled prior to use.

Graft copolymerization

FEP film (2 cm × 2 cm) of 75 μm thickness was washed with acetone and dried in oven at 50°C before use. Weighed amount of FEP was placed in a glass ampule containing varied percentage of monomer (10–35%) in different solvents. The ampule was irradiated for a total dose of 35 kGy at a dose rate of 4.92 kGy/h. Prior to irradiation the solution was purged with dry nitrogen.

For evaluation of the effect of total dose on percentage of grafting, monomer concentration was maintained at 20% in different solvents, and the solution was exposed to varied total dose (10–35 kGy). Low grafting yield cases (in presence of cyclohexanol, benzyl alcohol, and nitromethane) observed from concentration effects are not incorporated in the study. Irradiation was carried out in a gamma chamber 5000 provided by BRIT (India). The grafted films were freed from homopolymer by extracting with acetone–water mixture (1 : 1, v/v) in Soxhlet apparatus, for 72 h till constant weight of the samples was obtained.

Percentage of grafting was determined from the following expression:

$$\text{Percentages of grafting} = (w_1 - w_0)/w_0$$

where w_1 and w_0 are the weights of grafted film after complete removal of homopolymer and original film, respectively.

Characterization techniques

The chemical changes occurring in the FEP film upon grafting was investigated by FTIR. Spectra of the samples were recorded using a Perkin–Elmer 1650 FTIR spectrophotometer with a resolution of 4 cm⁻¹.

TGA studies were carried out using a TA instrument Hi-Res TGA 2950 thermogravimetric analyzer. The samples were heated from ambient temperature to 800°C at a heating rate of 20°C/min in nitrogen atmosphere. The samples selected for TGA analysis are the ones obtained from the grafting medium of dioxane–water binary mixture.

Dynamic mechanical properties of the samples were studied in a Rheometric scientific DMTA 3E Mark instrument. The test was carried out in the dynamic temperature ramp module in the rectangular tension mode. The dimensions of the sample were 5 mm in width and 10 mm in length. Samples

TABLE I
Solubility Parameter of Solvents and Solvent Pairs

Solvent	Solubility parameter, δ (cal cm ⁻³) ^{1/2}
THF	9.1
MEK	9.3
Acetone	9.9
Dioxane	10
4-Vinyl pyridine	11.0
Isopropanol + MEK (86 : 14 wt %)	11.2
Cyclohexanol	11.4
Isopropanol	11.5
Benzyl alcohol	12.1
Nitromethane	12.2
Ethanol	12.9
Ethanol + water (92 : 8 wt %)	13.4
Methanol	14.5
Acetone + water (1 : 1, v/v)	15.5
Dioxane + water (1 : 1, v/v)	16.7
Water	23.4

were scanned from 50 to 200°C at the heating rate of 5°C/min at a fixed frequency of 1 Hz.

Surface and cross section of a grafted films with different percentage of grafting, prepared from dioxane–water binary mixture, were analyzed by X-ray mapping for distribution of nitrogen. The measurements were carried out at a 10 kV electrical high tension using an SEM microscope (LEO 1450 model) equipped with an energy dispersive detector.

The surface free energies of grafted samples were determined by contact angle goniometry in a thermostated cell (20°C ± 1°C) using a Kruss G10 Goniometer interfaced to image capture software. Advancing (θ_A) contact angles were measured for droplets (2–10 μL) of doubly distilled water and diiodomethane.

RESULTS AND DISCUSSION

Table I gives the three-dimensional solubility parameter of solvents²⁷ and binary mixture of solvents used in the grafting reaction. Solubility parameter of the binary mixtures has been calculated as per the equation:

$$\delta_{\text{mix}} = \frac{\delta_1 X_1 V_1 + \delta_2 X_2 V_2}{X_1 V_1 + X_2 V_2}$$

where δ_{mix} is the solubility parameter of a mixture of solvents; X_1 and X_2 are molar fractions of components 1 and 2; V_1 and V_2 are the molar volumes of components 1 and 2; δ_1 and δ_2 are the solubility parameters of components 1 and 2.

Figure 1 shows the effect of monomer concentration on percentage of grafting. The same for low yield grafting cases has been represented in Figure 2. From Figure 1 it is seen that the percentage of

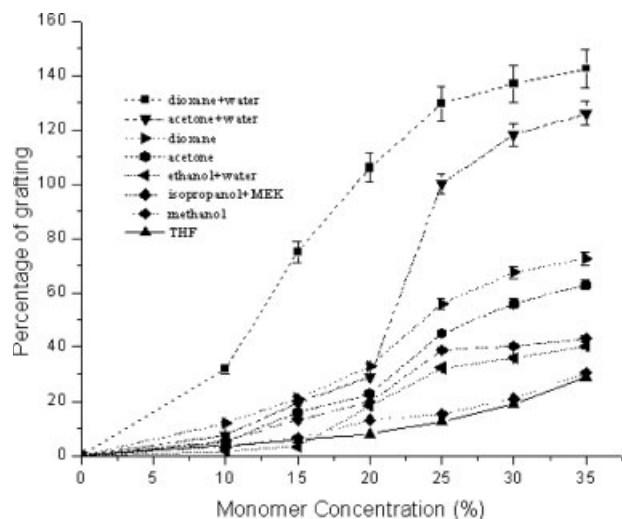


Figure 1 Effect of monomer concentration on percentage grafting at a fixed total dose of 35 kGy, irradiated at a dose rate of 4.92 kGy/h.

grafting initially increases with monomer concentration, followed by a sudden upward jump, marking the onset of autoacceleration or Tromsdorff effect. With further increase in monomer concentration, the percentage of grafting plateaus. This pattern in grafting has been reported for grafting of vinyl monomers onto various substrates.²⁸ Furthermore, it is observed that autoacceleration onsets at different concentrations for different solvent systems. For dioxane–water and acetone–water binary mixtures the onset is at 10% monomer concentration. For the rest of the solvent systems the onset occurs at 15–20% of monomer concentration. Furthermore it is observed that the degree of grafting decreases in the following order: dioxane–water > acetone–water > dioxane > acetone > ethanol–water > isopropanol–MEK > methanol > THF.

It has been established that the grafting of vinyl monomers in FEP occurs by frontal mechanism. Grafting starts from layers close to the surface, then proceeds inwardly toward the core of the film by progressive diffusion through the swollen grafted layers.^{22,29} Hence, best and uniform grafting is expected to occur in a solvent system in which the solubility parameter of solvent is closer to the monomer or polymer. Thus, according to Yang and Hsui,³⁰ grafting of 4-vinyl pyridine onto styrene–butadiene–styrene triblock copolymer in methanol yielded better grafting than in ethanol because of the close proximity of the solubility parameter of methanol-based system with poly(4-vinyl pyridine) than the ethanol-based system. Similar views have been provided by Kang et al.³¹ in grafting of styrene onto PTFE. However, in the present case, the percentage of grafting is lower in dioxane as well as in acetone

(despite having closer proximity of solubility parameter) compared with their corresponding mixture in water (Table I). From these observations it is clear that percentage of grafting cannot be explained merely based on solubility parameter. Another parameter such as chain transfer to solvent also influences grafting. It appears that water as a reaction medium is a very good solvent for graft copolymerization because it has a zero chain transfer constant, thus minimizing the wastage of monomer. Kaur et al.²⁶ have observed an increase in the degree of grafting of 4-vinyl pyridine onto FEP with increasing water content in alcohol/water mixture. It is clear from the observation made in present case that not only solubility parameter but also chain transfer to solvent and wetting of the solution mixture with the substrate chosen for grafting are other important factors which affect the grafting efficiency as well.

To account for the onset of autoacceleration at different concentrations for different solvent systems, it is well known that the rate of polymerization is very high when the chain transfer constant is minimum. Marked Tromsdorff effect has been observed in solvents pairs such as dioxane–water and acetone–water. Dioxane–water being not a good solvent, the chain transfer constant is not much affected because of combined effect of limited swelling and minimum chain transfer.

Figure 2 represents the effect of monomer concentration on percentage of grafting for low-yield cases. Cyclohexanol has a solubility parameter of $11.4 \text{ (cal/cm}^3)^{1/2}$, which is in close approximation with poly 4-vinyl pyridine itself. However, low grafting is due to the higher chain transfer constant of cyclohexanol. Similar trend is observed in the presence of benzyl

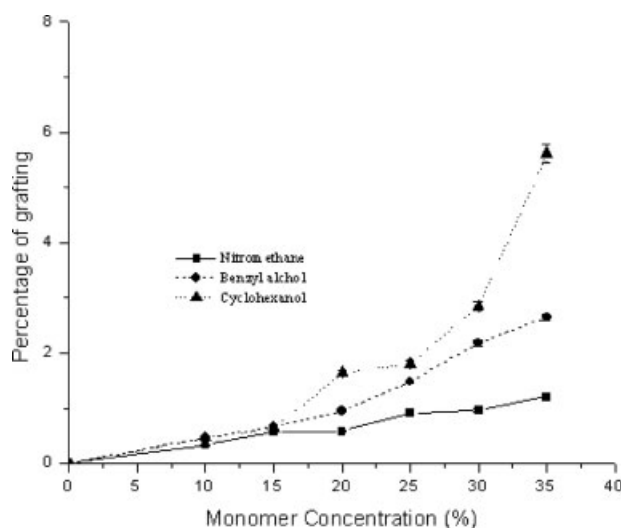


Figure 2 Effect of monomer concentration on percentage grafting (low yield cases) at a fixed total dose of 35 kGy, irradiated at a dose rate of 4.92 kGy/h.

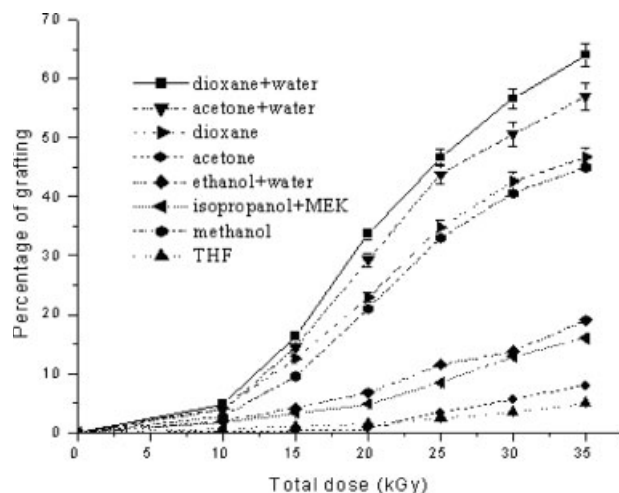


Figure 3 Effect of total dose on percent grafting at 20% monomer concentration irradiated at a dose rate of 4.92 kGy/h.

alcohol. It is known that the alcohols having high chain transfer constant values accelerate various chain transfer reactions leading to premature termination of growing polymer chains that causes a decrease in percentage of grafting. Similar observations have been made by others.²⁵ In the presence of nitromethane, nitro group probably scavenges the growing radicals, lowering the grafting yield. Garnett and Martin²⁵ have observed that cyclohexanol, benzyl alcohol, and nitromethane were nonpromoters of grafting of 4-VP.

Figure 3 shows the effect of total dose on percentage of grafting. In this study the low grafting yield solvent systems have been deliberately excluded. In this case it is observed that the order of grafting follows the similar trend as observed in the case of effect of monomer concentration. Furthermore, it is observed that at a fixed monomer concentration of 20%, autoacceleration occurs at a total dose of 10 kGy for the binary mixtures of dioxane–water and acetone–water, whereas the effect is less pronounced in other cases.

Evidence of grafting

FTIR spectroscopy

Figure 4 shows the FTIR spectra of FEP and FEP-g-4-VP samples prepared from binary mixture of dioxane and water. From the figure it is seen that both FEP and graft copolymers show a broad band at 1150–1250 cm^{-1} because of the stretching of CF_2 groups. A sharp peak at 981 cm^{-1} is also noticed, attributable to the C–F stretching of CF_3 group in the substrate as well as graft copolymers. Appearance of new bands is observed in the graft copolymers. A peak at 1493 cm^{-1} due to $-\text{C}=\text{N}$ for pyridine ring of FEP-g-4-VP is seen to be present. With increasing

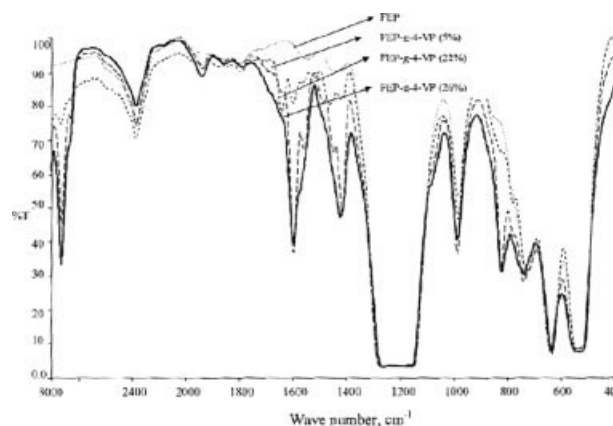


Figure 4 FTIR spectra of FEP and FEP-g-4-VP samples obtained from dioxane–water binary mixture as solvent by varying the total dose.

percentage grafting, the intensity of the peak increases, as expected. Further the graft copolymers show sharp peak at 2943 cm^{-1} due to the aliphatic $-\text{CH}_2$ stretching of 4-vinyl pyridine-grafted chains.

Thermogravimetric analysis

Figure 5 shows the TGA plot of FEP and FEP-g-4-VP samples with varying percentage of grafting prepared from dioxane–water binary mixture. From the figure it is seen that FEP has an initial decomposition temperature (IDT) of 436°C, whereas the grafted samples show a two-step degradation profile. The first step corresponds to the degradation of the grafted poly(4-vinyl pyridine) chains, followed by the degradation of FEP itself. The thermal stability data for the grafted films are illustrated in Table II. From the table it is seen that neat poly(4-vinyl pyridine) prepared from dioxane–water binary mixture at 35 kGy does show an IDT of 317°C. The IDT of the grafted samples are found to decrease with

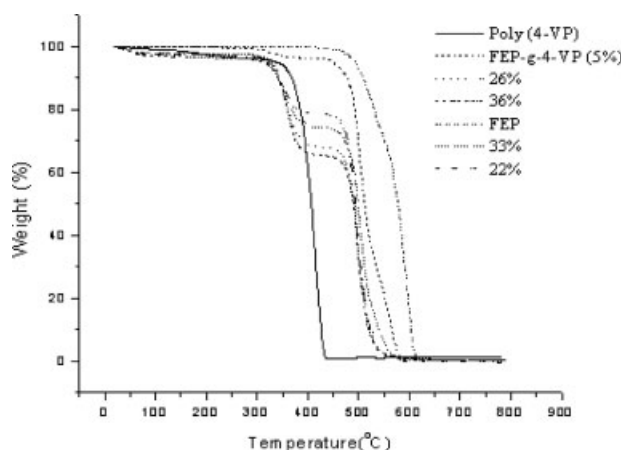


Figure 5 TGA analysis of FEP and FEP-g-4-VP samples obtained using dioxane–water binary mixture as solvent by varying total dose.

TABLE II
Thermal Stability of the FEP-g-4-VP Samples: TGA Experiments

Percentage of grafting	Step 1			Step 2	
	T_{ON} (°C)	T_{max} (°C)	Δm (wt %)	T_{ON} (°C)	T_{max} (°C)
0 (FEP)	436	516	–	–	–
5	307	354	4.2	347	501
22	300	352	21.6	352	498
26	284	356	25.2	354	596
33	282	358	32.1	353	494
36	279	357	35.4	356	494
Poly (4-VP)	317	415	99.8	–	–

T_{ON} , initial decomposition temperature; T_{max} , temperature at the maximum rate of weight loss; Δm , partial weight loss at the corresponding decomposition step.

increased percentage of grafting. This could be attributed to the fact that homopolymerized poly (4-vinyl pyridine) would grow to a higher molecular weight compared with the graft copolymers with a higher thermal stability. Furthermore, the partial weight loss in the first decomposition step implies that the percentage of grafting corresponds well with those determined from simple weight measurements. It is also observed that the thermal stability of FEP decreases with increase in grafting. This could be due to the radiation-induced degradation of FEP. To substantiate the possible radiation-induced degradation of FEP, the films were irradiated to total dose of 25 and 50 kGy and TGA analysis was carried for the irradiated films. Figure 6 illustrates the TGA of irradiated FEP samples. From the figure it is seen that for irradiated FEP samples, IDT shifts to lower temperature, indicating decrease in thermal stability.

Dynamic mechanical analysis

DMA of FEP and FEP-g-4-VP samples prepared from dioxane–water binary mixture are represented in Figure 7. It is seen that FEP has a sharp $\tan \delta$

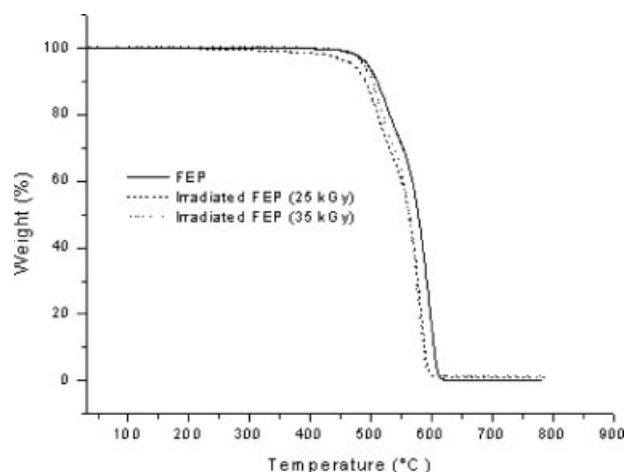


Figure 6 TGA analysis of radiation-treated FEP samples.

peak at 90°C, corresponding to its glass transition temperature. With increasing grafting, the $\tan \delta$ maximum shifts to higher temperature, with progressive increase in the intensity of peaks as well. The increasing intensity of the $\tan \delta$ peak is clearly due to the incorporation of glassy 4-vinyl pyridine chains onto FEP. At 18% of grafting a shoulder peak is observed in the $\tan \delta$ peak. This indicates that at 18% of grafting of poly 4-VP, grafting is not homogeneous. Beyond 18% grafting no shoulder peak is observed. The appearance of single peaks in the DMA plot for varied grafting levels suggest that the 4-vinyl pyridine is covalently bonded to the FEP. Beyond 35% grafting the DMA analysis was not possible as the films became brittle with the incorporation of glassy 4-vinyl pyridine chains.

SEM-EDAX

The area of X-ray mapping of the grafted film (35%) for elemental nitrogen contributed by grafted poly(4-vinyl pyridine) is shown in Figure 8. From the figure

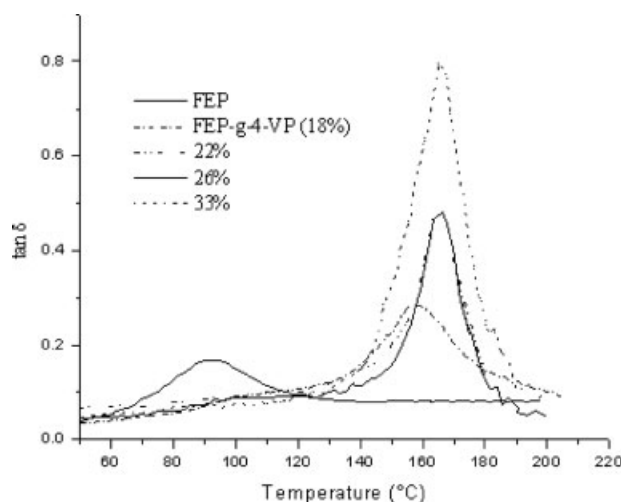


Figure 7 Dynamic mechanical analysis of FEP and FEP-g-4-VP samples obtained using dioxane–water binary mixture as solvent by varying the total dose.

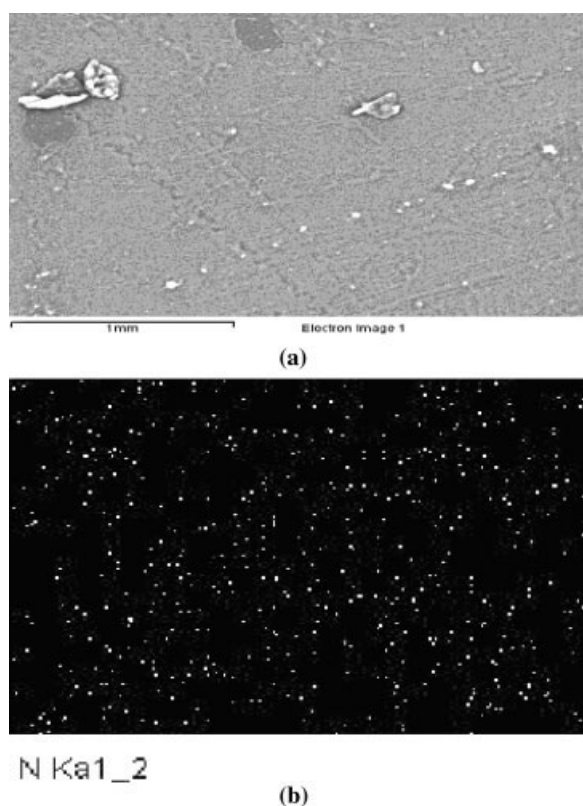


Figure 8 (a) SEM micrograph of FEP-g-4-VP surface (36% grafting) obtained using dioxane–water binary solvent mixture. (b) X-ray mapping for distribution of nitrogen (EDAX) in FEP-g-4-VP surface (36% grafting) obtained using dioxane–water binary solvent mixture.

it is observed that the white dots representative of nitrogen are uniformly distributed, indicating uniform grafting. Depth profiling of a few representative grafted samples were carried out by X-ray mapping the elemental nitrogen across the cross section of a few grafted samples. Figure 9 shows the SEM-EDAX pictures of a few grafted samples. From the figure it is observed that at 5% grafting, only a few micron depth on either side of the base polymer shows the presence of nitrogen, contributed by the grafted 4-vinyl pyridine chains. As the grafting percentage increases, the grafting front propagates reaching the bulk of the sample. At 36% grafting, uniform distribution of the elemental nitrogen is seen, implying uniformity of grafting across the thickness of the base polymer.

Surface energy

Surface energies were evaluated using the surface tension-component theory. According to this approach, the surface tension of a phase could be divided up into independent components such as London dispersions contribution γ^d and polar contribution γ^p , as represented below.

$$\gamma = \gamma^d + \gamma^p$$

For a drop of liquid at equilibrium with a solid surface, the liquid–solid contact angle (θ) is given by the following equation:

$$\gamma_L(1 + \cos \theta)/2(\gamma_L^d)^{1/2} = (\gamma_S^p)^{1/2}(\gamma_L^p \gamma_L^d)^{1/2} + (\gamma_S^d)^{1/2}$$

where γ_L is the surface tension of the liquid and subscript S = solid and L = liquid. γ_L , γ_L^d , and γ_L^p can be found in literature.³² In this study, diiodomethane and water were used as the probing liquids. For water, $\gamma_L = 72.8 \text{ mJ/m}^2$, $\gamma_L^p = 51.0 \text{ mJ/m}^2$, and $\gamma_L^d = 21.8 \text{ mJ/m}^2$. For diiodomethane, $\gamma_L = 50.76 \text{ mJ/m}^2$,

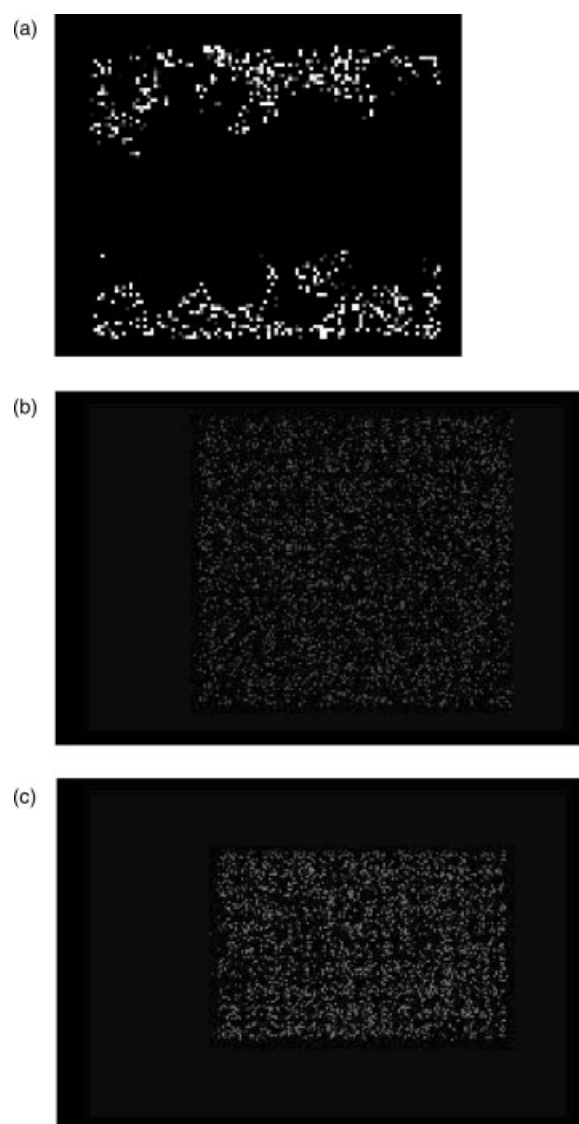


Figure 9 (a) X-ray mapping for distribution of nitrogen (EDAX) in FEP-g-4-VP cross section (5% grafting). (b) X-ray mapping for distribution of nitrogen (EDAX) in FEP-g-4-VP cross section (26% grafting). (c) X-ray mapping for distribution of nitrogen (EDAX) in FEP-g-4-VP cross section (36% grafting).

TABLE III
Representative Advancing Contact Angles, Surface Energies, and the Polar and Disperse Components of FEP and FEP-g-4-VP Films

Percentage of grafting	Contact angle (°), water	Contact angle (°), CH ₂ I ₂	Surface energy, σ (mN/m)	Disperse component, σ_d (mN/m)	Polar component, σ_p (mN/m)
0 (FEP)	109 ± 2.2	91 ± 1.7	12.9 ± 0.8	11.8 ± 0.2	1.1 ± 0.3
5	95 ± 2.1	79 ± 1.5	19.5 ± 0.5	16 ± 0.2	3.5 ± 0.2
22	83 ± 1.5	73 ± 1.4	25.7 ± 0.4	17.6 ± 0.2	8.1 ± 0.2
26	76 ± 1.2	66 ± 1.2	32 ± 0.3	20.8 ± 0.2	10.2 ± 0.2
36	64 ± 1.3	53 ± 1.4	41 ± 0.3	26.7 ± 0.2	14.3 ± 0.2

$\gamma_L^p = 0 \text{ mJ/m}^2$, $\gamma_L^d = 50.76 \text{ mJ/m}^2$ at 20°C. Hence, by measuring the contact angle for two well-characterized liquids, two equations with two unknowns, i.e., γ_s^d and γ_s^p , are generated. The surface energy $\gamma_s = \gamma_s^d + \gamma_s^p$ can be obtained.

The advancing contact angles for two probing liquids of water and diiodomethane and total surface energy values with their polar and disperse components are illustrated in Table III. From the results it is seen that the base polymer FEP has an advancing contact angle of 109° and 91°, with water and diiodomethane, respectively. This corresponds to a surface energy of 12.9 mN/m with a polar and disperse component of 11.8 and 1.1 mN/m, respectively. Brack et al. reported³³ a surface energy value of 12.3 mN/m for FEP, by adopting acid–base component approach. The advancing contact angle for both water and diiodomethane decrease with increase in grafting. Consequently the surface energies show an increasing trend with increased grafting. It must be noted that the graft level is a bulk property and is averaged over film thickness and area, as already seen from SEM-EDAX studies. However, increase in grafting also results in higher concentration of polar 4-vinyl pyridine-grafted chains on the surface. The hydrogen bonding functional groups thus increase the total surface energy as well as the polar component of the surface energy as seen from the results.

CONCLUSIONS

The percentage of grafting in radiation-induced graft polymerization is affected by the selection of the solvent for grafting reaction. Grafting is governed by both chain transfer constant of solvent and solubility parameter. Grafting was observed to be higher in binary mixtures of dioxane–water and acetone–water, despite the overall solubility parameter is higher than that for poly(4-vinyl pyridine) because of low chain transfer constant. Water plays an important role in the grafting process, as is evident from the binary mixtures. This is probably due to its zero chain transfer constant. The graft copolymers have been characterized by FTIR, TGA, DMA, SEM-EDAX, and contact angle goniometry.

References

- Gupta, B.; Büchi, F.; Scherrer, G. G. *J Polym Sci Part A: Polym Chem* 1994, 32, 1931.
- Gupta, B.; Scherrer, G. G. *Chimia* 1994, 48, 127.
- Vigo, F.; Capenelli, G.; Uliana, C.; Munara, S. *Desalination* 1981, 36, 63.
- Nasef, M.; Saidi, H.; Nor, H. *J Appl Polym Sci* 2000, 76, 220.
- Niemöller, A.; Ellinghorst, G. *Makromol Chem* 1987, 148, 1.
- Rouilly, M.; Kötz, E.; Haas, O.; Scherrer, G. G.; Chapiro, A. *J Membr Sci* 1993, 81, 89.
- Gupta, B.; Büchi, F.; Scherrer, G. G.; Chapiro, A. *J Membr Sci* 1996, 118, 231.
- Gupta, B.; Büchi, F.; Staub, M.; Graman, D.; Scherrer, G. G. *J Polym Sci Part A: Polym Chem* 1996, 34, 1873.
- Nasef, M.; Saidi, H.; Nor, H. M.; Ooi, M. F. *J Appl Polym Sci* 2000, 76, 1.
- Gupta, B.; Chapiro, A. *Eur Polym J* 1989, 25, 1145.
- Patri, M.; Hande, V. R.; Phadis, S.; Deb, P. C. *Polym Adv Technol* 2004, 15, 485.
- Kabanov, V.; Sidorova, L.; Spitsyn, V. *Eur Polym J* 1974, 10, 1153.
- Kotsov, G.; Turmanova, S. *J Appl Polym Sci* 1997, 64, 1469.
- Kaur, I.; Gupta, A.; Misra, B. N.; Chauhan, G. S. *Desalination* 1997, 110, 115.
- Kaur, I.; Barsola, R.; Misra, B. N. *J Appl Polym Sci* 1995, 56, 1197.
- Elmidaoui, A.; Belcadi, S.; Houdus, Y.; Cohen, T.; Gavach, C. *J Polym Sci Part A: Polym Chem* 1992, 30, 1407.
- Dessouki, A.; Hegazy, E. S.; El-Dessouky, M.; El-Sawy, N. *Radiat Phys Chem* 1985, 26, 157.
- Nasef, M.; Hegazy, E. S. *Prog Polym Sci* 2004, 29, 499.
- Dworjain, P. A.; Ganett, J. L. *Prog Polym Sci* 1992, 3, 93.
- Kabanov, V.; Aliev, R.; Sidorova, L. *J Polym Sci Polym Chem Ed* 1980, 18, 871.
- Gupta, B.; Anjum, N.; Gupta, A. P. *J Appl Polym Sci* 2000, 77, 1401.
- Walsby, N.; Paronen, M.; Juhoanoja, J.; Sundholm, F. *J Polym Sci Part A: Polym Chem* 2000, 38, 1512.
- Machi, S.; Kamel, I.; Silverman, J. *J Polym Sci Part A-1: Polym Chem* 1970, 8, 3329.
- El-Nesr, E. *J Appl Polym Sci* 1997, 63, 377.
- Garnett, J. L.; Martin, E. C. *Aust J Chem* 1976, 29, 2591.
- Kaur, I.; Misra, B. N.; Kohli, A. *Desalination* 2001, 139, 357.
- Beerbower, A.; Hansen, C. M. *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl Vol., 2nd ed.; Wiley Interscience: New York, 1969.
- Dragavillie, T.; George, G.; Niemoeller, A.; Hill, D.; Whittkar, A. *Progr Polym Sci* 2003, 28, 1355.
- Nasef, M. *Polym Int* 2001, 50, 338.
- Yang, J.; Hsui, G. *J Appl Polym Sci* 1990, 39, 1475.
- Kang, K.; Kang, P. H.; Nho, Y. C. *J Appl Polym Sci* 2006, 99, 1415.
- Heather, R. *Progress on Rubber and Plastics Technology*; IOM/RAPRA: UK, 1997.
- Brack, H. P.; Wyler, M.; Peter, G.; Scherer, G. G. *J Membr Sci* 2003, 214, 1.